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ORIGINAL PAPER

A Novel Hydrogen-Bonded 3D Network with Unusual Coordination Mode

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Abstract A hydrogen-bonded 3D network $[Mn(H_2O)_2(nbdc)]_n$, **1** H_2nbdc = 2-aminoterephthalic acid) crystallizes in the monoclinic, space group $P2_1/c$, $a = 9.6418(6)$, $b = 6.4491(4)$, $c = 15.3216(9)$ Å, $\beta = 95.792(1)°$, $Z = 4$ and displays unusual coordination mode (Mn–N (from nbdc), 2.275(3) Å). In the structure of **1**, the Mn^{2+} ions are connected with μ_2-carboxylates to form left handed and right handed chiral helix chains $(–Mn–O–C–O–)_n$, which are connected by nbdc ligands to form 2D sheet along *b* axis, then these 2D sheets are further linked together through Mn–OH_2···O (from μ_2 carboxylate) –Mn hydrogen–bonds to construct the 3D network.

Keywords Hydrogen-bond · 3D network · Crystal structure · Photoluminescence

Introduction

The design and syntheses of extended supramolecular networks with predefined connectivity and dimensionality constitutes a major challenge for chemists [1–9]. Metal–organic coordination polymers also have attracted great interest because of their interesting properties, potential applications and novel topologies [10–22]. Rationally designed organic ligands and properly selected metal ions are the key roles for construct intriguing and useful coordination polymers [23, 24]. The investigation of coordination polymers with aromatic carboxylates and their derivatives have obtained rapid development in recent years [25–51], the various structures and interesting properties have been discovered to be determined by the substituents [20–22, 25–27]. Systematic studies on coordination polymers with H_2nbdc have been reported [27–37]. However, to the best of our knowledge, coordination polymers with M–N(from nbdc) are rarely reported [49–51]. Herein we report a novel hydrogen-bonded 3D network structure with an unusual coordination mode Mn–N 2.275(3)Å (N from nbdc, H_2nbdc = 2-aminoterephthalic acid).

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Experimental

Materials and Methods

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. IR (KBr) was performed on Nicolet 740 FTIR Spectrophotometer; the range of λ is 4000–400 cm^{-1}. Elemental analysis was carried out on a CE instruments EA 1110 elemental analyzer. Photoluminescence was performed on a Hitachi F-4500 Fluorescence Spectrophotometer. X-ray powder diffraction was measured on a Panalytical X-Pert pro diffractometer with Cu Kα radiation.

Synthesis

$[Mn(H_2O)_2(nbdc)]_n$ **1**, H_2nbdc (0.091 g, 0.50 mmol) and NaOH (0.040 g, 1.0 mmol) were dissolved in deionized

H_2O (10 mL), nitric acid (2 mol/L) was slowly added to the solution until pH was adjusted to 7, then $MnCl_2{\cdot}4H_2O$ (0.099 g, 0.50 mmol) was added. The mixture was filtrated, and the filtrate was left to stand in air. After 2 weeks, brown block crystals (0.036 g, yield 27%) were separated by filtration, washed with deionized water and dried in air. Elemental Analysis: $C_8H_9NO_6Mn$, found (calc.) C 34.96 (35.57), H 3.29 (3.33), N 5.11 (5.18)%. FTIR (KBr, cm^{-1}): 3487 (m),3353 (s), 3129 (w), 1618 (m), 1559 (vs), 1418 (m), 1380 (vs), 1304 (w), 1237 (w), 951 (w), 840 (m), 774 (s).

Table 1 Crystal data for **1**

Empirical formula	$MnC_8H_9NO_6$
Formula weight	270.10
Crystal size (mm)	0.18 × 0.16 × 0.08
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.6418(6)
b (Å)	6.4491(4)
c (Å)	15.3216(9)
α (°)	90
β (°)	95.792(1)
γ (°)	90
V(Å^3)	947.85(10)
T(K)	296(2)
Z, D_{calcd} (Mg/m^3)	4, 1.893
F(000)	548
μ(mm^{-1})	1.406
h_{min}/h_{max}	−12/12
k_{min}/k_{max}	−8/8
l_{min}/l_{max}	−19/20
Ref. collected/unique	7683/2205
R_{int}	0.0275
Parameters	181
Max/min transmissions	0.8958/0.7859
Final R indices[$I > 2\sigma(I)$]	$R_1 = 0.0537$, $wR_2 = 0.1124$
R indices (all data)	$R_1 = 0.0575$, $wR_2 = 0.1145$
Goodness-of-fit on F^2	1.133
Max./min., $\Delta\rho$ (e·Å^{-3})	0.608/−0.395
Completeness (%)	99.8

$R_1 = \Sigma| |F_o| - |F_c| |/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$

X-ray Crystallography

Data collection for **1** was performed on a Bruker SMART Apex CCD diffractometer at 296 K with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Absorption correction was applied by using the multi-scan program SADABS [47]. The structure was solved by direct method, and non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program [48]. Crystal data as well as details of data collection and refinement for **1** are summarized in Table 1, and selected bond lengths and angles for **1** are shown in Table 2.

Result and Discussion

Compound **1** was synthesized as brown block crystals by the reaction of $MnCl_2{\cdot}4H_2O$ and H_2nbdc under room-temperature. Single crystal X-ray analysis has revealed that there are one Mn^{2+}, one nbdc and two water molecules in the asymmetric unit (Fig. 1). The Mn^{2+} lies in a slightly distorted octahedral coordination environment, coordinated by two oxygen atoms from two μ_2-carboxyls (Mn1–O1 2.155(2), Mn1–O2b 2.221(2) Å), one oxygen atom from a monodentate carboxyl (Mn1–O3a 2.151(2) Å), two oxygen atoms from two water molecules (Mn1–O1W 2.197(3), Mn1–O2W 2.221(3) Å) and one nitrogen atom from nbdc (Mn1–N1 2.275(3) Å). The Mn^{2+} ions are connected by μ_2-carboxyls to form left handed and right handed chiral helix chains $(–Mn–O–C–O–)_n$ along a axis (Fig. 2), which are connected by nbdc ligands in ab plane to form 2D sheet (Fig. 3). Then these 2D sheets further stack in AA mode

Table 2 Selected bond lengths (Å) and angles (°) for **1**

Mn1–N1	2.275 (3)	O1–Mn1–N1	77.56 (10)	O3^a–Mn1–O2^b	175.68 (9)
Mn1–O1	2.155 (2)	O1–Mn1–O2^b	92.33 (9)	O3^a–Mn1–O1W	89.78 (10)
Mn1–O2^b	2.221 (2)	O1–Mn1–O1W	177.16 (11)	O3^a–Mn1–O2W	90.72 (9)
Mn1–O3^a	2.151 (2)	O1–Mn1–O2W	87.03 (10)	O1W–Mn1–N1	105.10 (12)
Mn1–O1W	2.197 (3)	O2^b–Mn1–N1	93.65 (9)	O1W–Mn1–O2^b	86.54 (10)
Mn1–O2W	2.221 (3)	O2^b–Mn1–O2W	87.04 (9)	O1W–Mn1–O2W	90.32 (12)
O2–Mn1^c	2.221 (2)	O3^a–Mn1–N1	89.50 (10)	O2W–Mn1–N1	164.59 (11)
O3–Mn1^d	2.151 (2)	O3^a–Mn1–O1	91.25 (9)		

Symmetry codes: ^{a} −x + 1, y − ½, −z + 1/2; ^{b} −x, y + 1/2, −z + ½; ^{c} −x, y − ½, −z + ½; ^{d}−x + 1, y + ½, −z + ½

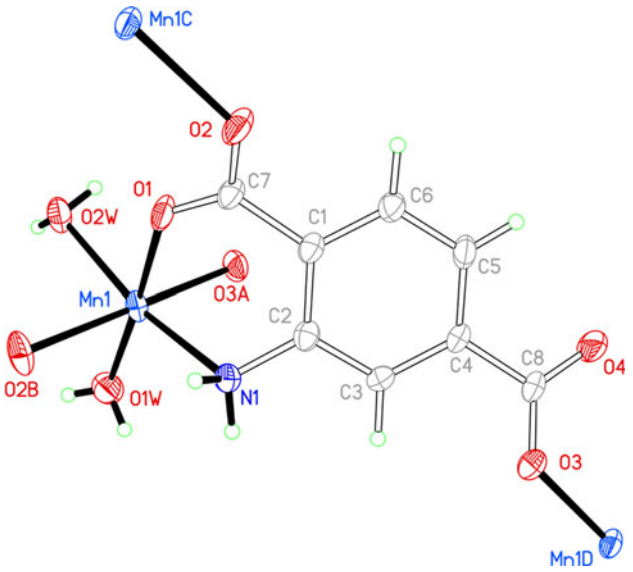

Fig. 1 *ORTEP* plot at 50% probability showing the coordination environment of manganese ion in **1**. Symmetry codes: A: −x + 1, y − ½, −z + ½; B: −x, y + ½, −z + ½; C: −x, y − ½, −z + ½; D: −x + 1, y + ½, −z + ½

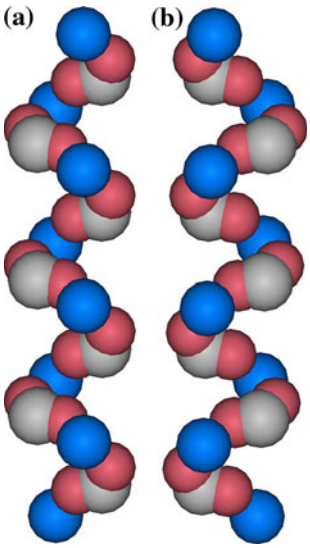

Fig. 2 **a** The left handed and **b** right handed chiral helix chains of $Mn(CO_2)_n$ in the 2D sheets

through the Mn–OH_2···O (from μ_2-carboxylate) hydrogen-bonds to form 3D network along *b* axis (Fig. 4).

X-ray powder diffraction measurement and elemental analysis show that the pure phase of **1** has been obtained. The most significant feature in the structure of **1** is the unusual coordination mode (Mn–N (from nbdc), 2.275(3) Å). The formation of the unusual coordinated bond present in **1** is due to the stable six member ring (–Mn–N–C–C–C–O–). In the structure of **1**, hydrogen-bonds play key role in the formation of the 3D network (Table 3). The solid state

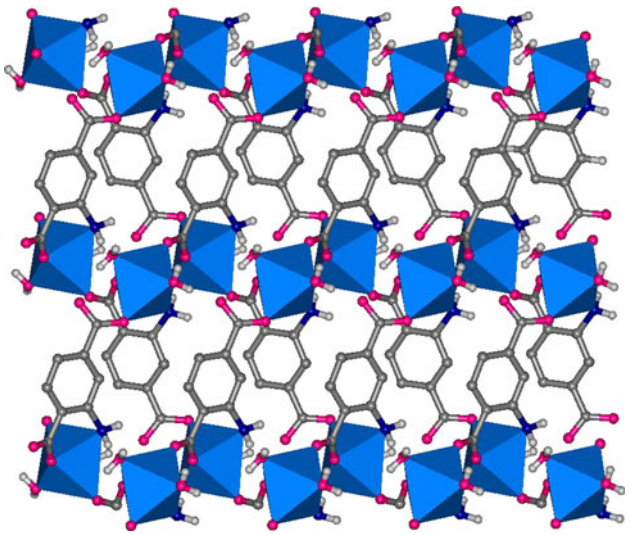

Fig. 3 A perspective view of the 2D sheets of **1** along *c* axis (Hydrogen atoms are omitted for clarity)

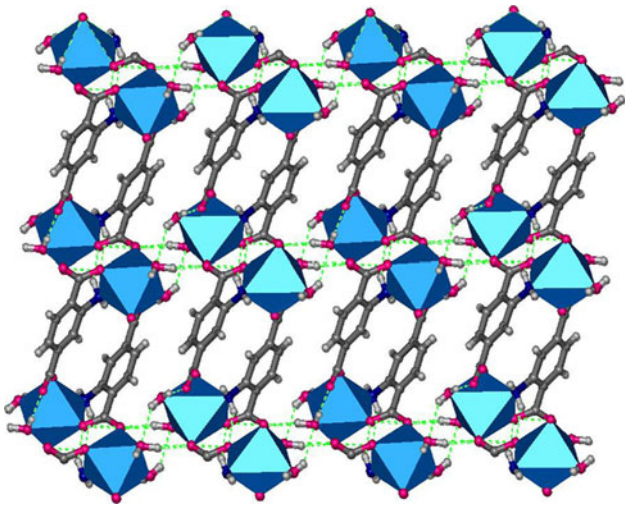

Fig. 4 View of hydrogen-bonded 3D network structure of **1** along *b* axis

Table 3 Hydrogen-bonding geometry for **1** (Å and °)

D–H···A	d(D···A)	∠(DHA)
O1W–H1A···O4[d]	2.658 (4)	174 (5)
O1W–H1B···O2W[e]	2.881 (4)	147 (7)
O2W–H2A···O2[d]	2.754 (4)	166 (5)
O2W–H2B···O4[a]	2.654 (3)	164 (5)
N1–H1···O4[d]	3.101 (4)	138 (4)
N1–H2···O1[b]	2.834 (4)	152 (4)

Symmetry codes: [a] −x + 1, y − ½, −z + 1/2; [b] −x, y + 1/2, −z + ½; [c] −x, y − ½, −z + ½; [d] −x + 1, y + ½, −z + ½; [e] −x, −y + 1, −z + 1

IR spectrum of **1** shows that there are four strong bands between 774 and 3,487 cm^{-1}: the anti-symmetric stretching vibration and symmetric stretching vibration of $–NH_2$ appear at 3,487 and 3,353 cm^{-1}, respectively; the stretching vibration of C–H in phenyl appears at 3,129 cm^{-1}; the asymmetric carboxylate stretching vibration at 1,618 and 1,559 cm^{-1} (very strong) and symmetric carboxylate stretching vibration at 1,418 cm^{-1}; strong stretching vibration of C–N at 1,380 cm^{-1} and strong C–H out-planar vibration in phenyl at 774 cm^{-1} [43, 44]. In the solid state, both **1** and nbdc emit blue fluorescence at 421 nm upon photoexcitation at 320 nm, but the intensity of **1** is stronger than H_2nbdc. The emissions may be assigned as π^*–n transfer [45, 46].

Supplementary Material

CCDC No. 673848 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge via (please use the link below) by e-mailing data_request@ccdc.cam.ac.uk, or by contacting: The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223 − 336033. www.ccdc.cam.ac.uk/data_request/cif.

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